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(54) Title: ONLINE MEASUREMENT OF CRYSTALLINITY IN SEMICRYSTALLINE POLYMERS BY RAMAN SPECTROSCOPY

(57) Abstract

A method for online measurement of crystallinity of semicrystalline polymers by illuminating oneline a sample of the polymer with a beam of light, collecting scattered light, converting the collected scattered light to a Raman spectrum, and determining the degree of crystallinity using the Raman spectrum. Further, a method for process control of the crystallinity of a semicrystalline polymer by adjusting online the crystallinity of the semicrystalline polymer according to the online measurement of crystallinity.

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ONLINE MEASUREMENT OF CRYSTALLINITY IN SEMICRYSTALLINE POLYMERS BY RAMAN SPECTROSCOPY

This invention relates to a novel method for online measurement of crystallinity in semicrystalline polymers, more particularly by Raman spectroscopy. More specifically, the present invention relates to the online use of Raman spectroscopy to monitor and control the crystallinity during the production of semicrystalline polymers such as syndiotactic polystyrene.

Crystalline polymers are pervasive in today's society. As is well known, crystalline polymers are not fully ordered, but are partially, or semicrystalline. Practically all physical and mechanical properties of semicrystalline polymers are strongly effected by the degree of crystallinity, such as higher temperature resistance and better solvent resistance. Therefore, the ability to measure and control the degree of crystallinity of semicrystalline polymers on production equipment during their manufacture, sometimes referred to as online, is of paramount importance.

Online measurement of crystallinity of polymers has been performed by wide angle X-ray diffraction and birefringence measurements. Wide-angle X-ray diffraction affords a direct determination of crystallinity, but this method is tedious and requires relatively large amounts of experimental data. Thus, online wide-angle X-ray diffraction is less economically practical in a production plant environment. Birefringence measurement depends on opacity of a sample. Opacity measurement depends on the geometry of the sample, that is pellets or strands, as well as the size of the polymer crystallites relative to the wavelength of the light source. While birefringence measurement is more economically suited for production plant environments than wide-angle X-ray diffraction, the opacity/geometry dependence introduces variability and limits its reproducibility, reliability and therefore its usefulness.

Other methods are known to determine the degree of crystallinity, but do not necessarily measure the same degree of crystallinity. Like birefringence techniques, these other methods measure properties related to the degree of crystallinity and do not afford a direct determination as does wide-angle X-ray diffraction. Differential scanning calorimetry ("DSC") determines heats of fusion, volumetric methods compare the density of a polymer that crystallizes to the densities of the completely crystallized polymer and that of the completely amorphous polymer, nuclear magnetic resonance ("NMR") method measures the fraction of immobile protons, and infrared and Raman spectra rarely involve true crystallinity bands, rather bands associated with regularity or preferred conformations. For a variety of

reasons these methods have not lent themselves to online measurement of crystallinity of semicrystalline polymers.

Historically, Raman spectroscopy equipment has been expensive and relative insensitive. The advent of lasers and fiber optics along with improvements in detectors and optical filters have all combined to make Raman spectroscopy more economical, sensitive, and suitable for some process applications. Online uses of Raman spectroscopy have been documented. Relative concentrations of organics in distillation streams is described by R. Arocs et al. in Vib. Spectra Structure, Vol. 19, p. 55-112 (1991), monitoring of semiconductor layer growth is described by V. Wagner et al. in Journal of Applied Physics, Vol. 10, No. 11, p. 7330-7333 (1994), monitoring reactions, such as the high speed cationic polymerization of divinyl ethers is described by E.W. Nelson et al. in Polym. Mater. Sci. Eng., Vol. 72, p. 413-414 (1995), and species generation during PCl_3 production is described by T.J. Vickers et al. in Appl. Spectrosc. Rev., Vol. 24, No. 4, p. 339-373 (1991).

It would be a further advance in the art of real time polymer process control to be able to determine online the degree of crystallinity of a semicrystalline polymer by a method which is economical, accurate, and reproducible. Preferably, the method would be independent of variables such as sample geometry.

The present invention is an economical, accurate, and reproducible method to measure online crystallinity of semicrystalline polymers by Raman spectroscopy. The method for online measurement of crystallinity of semicrystalline polymers comprises the steps of:

- (a) illuminating online a sample of the polymer with a beam of light;
- (b) collecting scattered light;
- (c) converting the collected scattered light to a Raman spectrum; and
- (d) determining the degree of crystallinity using the Raman spectrum.

In one embodiment of this invention, the step of determining the degree of crystallinity comprises:

- (i) integrating a crystalline-sensitive vibrational band of the Raman spectrum, which band is unique to a polymorph of the semicrystalline polymer, to obtain an integrated crystalline-sensitive vibrational band ("I_c");
- (ii) integrating a reference vibrational band of the Raman spectrum, whose intensity is not influenced by the degree of crystallinity of the semicrystalline polymer, to obtain an integrated reference vibrational band ("I_r"); and

(iii) ratioing I_c with I_i to determine the degree of crystallinity.

Another embodiment of this invention is the beam of light illuminates a strand, pellets, a film, fibers, or powder of the semicrystalline polymer. Further, the beam of light is laser light. A further embodiment of this invention is the steps of illuminating online and collecting 5 scattered light are performed with a Raman fiber optic probe. Yet a further embodiment of this invention is the semicrystalline polymer is syndiotactic polystyrene ("SPS").

Further investigations led to the discovery of a method for process control of the degree of crystallinity of a semicrystalline polymer by adjusting according to the online measurement of crystallinity. Preferably, the crystallinity of the semicrystalline polymer is 10 adjusted by controlling the temperature of the semicrystalline polymer. These and other features, aspects, and advantages of the present invention will become better understood with reference to the following description and amended claims.

A polymer solid can be partially crystalline, such as polyethylene, poly(ethylene 15 terephthalate), and syndiotactic polystyrene, or non crystalline such as polycarbonate, poly(methyl methacrylate), and atactic polystyrene. Partially crystalline polymers are constructed by a complicated aggregation of crystalline and amorphous regions. The weight fraction of the crystalline regions determines the degree of crystallinity. Thus, polymers having a degree of crystallinity greater than 0 and less than 100 are called semicrystalline. 20 In the crystalline region, polymer chains are extended in a definite characteristic structure and packed together regularly forming a crystallite.

For semicrystalline polymers, under the appropriate conditions of temperature, pressure, and stress or under the influence of solvents, a spontaneous ordering of the macromolecules or part of them can take place. When semicrystalline polymers are 25 crystallized from solution or cooling from the melt, they undergo crystalline transformation during which crystallinity, density, and hardness increase and the physical and thermal properties attain their ultimate values. The properties of semicrystalline polymers depend on chemical structure, molecular weight and molecular weight distribution, and the crystallization conditions. Control of the crystallization gives rise to a broad range of 30 properties, among which are the size of the crystallites, the degree of crystallinity, the molecular structure of the crystallites and the associated amorphous regions, and the polymer morphology.

Polymer crystallization occurs either from a deformed melt by the application of an external force or from an undeformed melt. Crystallization ordinarily takes place well below 35 the melting point of the semicrystalline polymer. The rate of crystallization is strongly

dependent on the crystallization temperature. Just below the melting temperature, the crystallization rate is low, but as the temperature is lowered, the rate increases and passes a maximum. At lower crystallization temperatures, the rate decreases again.

Semicrystalline polymers are manufactured in many forms, such as strands, pellets,

- 5 films, profiles, sheet, fibers, powders, or molded parts. Pellets are obtained by cutting extruded strands of semicrystalline polymer, either at a die face or remote from the die face, for example in a pelletizer. Extruded semicrystalline polymers may pass through air, a liquid bath, for example water, or a combination of the two. Preferably, the degree of crystallinity for a semicrystalline polymer can be controlled during manufacture by adjusting:
- 10 the melt temperature as the polymer exits the extruder, for example as a strand, film, or fiber, the air temperature surrounding the polymer, the bath temperature, the time the polymer is in the air, the time the polymer is in the bath, the rate the polymer is pulled through the extruder die, and combinations of two or more.

The instant invention is useful in determining the degree of crystallinity in

- 15 semicrystalline polymers. The semicrystalline polymers may be selected from a wide variety of such polymers, preferably, but not limited to polyethylene, polypropylene, polyethylene terephthalate, polybutylene terephthalate, polyethylene napthalene, polyamide, polyphenylene sulfide, and polyether ether ketone. In addition, these semicrystalline polymers may include various additives ordinarily incorporated into resins of this type. For
20 example, a filler, a reinforcing agent, a heat stabilizer, an antioxidant, a fire retardant, a plasticizer, an antistatic agent, a mold releasing agent, a blowing agent, or combinations of two or more can be used.

A Raman spectrum generally corresponds to frequencies of molecular vibrations and therefore can be related directly to molecular structure. In Raman spectroscopy, light, 25 preferably monochromatic light (excitation light) is generally directed onto a sample. Preferably, this monochromatic light is a single laser line. Most of the light scattered off the sample will be at the same wavelength as this laser line (Rayleigh scattering), but a portion of the light scattered off the sample will be scattered at wavelengths containing the sum or difference of the excitation and molecular vibrational frequencies (Raman scattering).

- 30 Optical fibers are advantageous in Raman spectroscopy. When optical fibers are used, light from a laser can be delivered to a sample via the fiber. After passage through the sample, the light back scattered from the sample can be collected by one or more other fibers and directed into a wavelength selective light detector, that is, a spectrometer. The advantages of using optical fibers in Raman spectroscopy include sampling remotely from
35 the spectrometer, sampling in a hostile environment and connecting several sampling

systems to a single detector. The primary disadvantage of using optical fibers is that Raman spectra may be generated from the optical fiber material itself, interfering with the Raman spectra of the sample. For example, if a silica-core fiber is used, the transmitted light will generate Raman spectra from the silica in the fiber. Part of this silica based Raman spectra, 5 along with part of the transmitted light, may be back scattered by the sample and enter the collecting optical fiber. The collected excitation light will generate additional silica Raman light as it traverses the collecting optical fiber. This silica based Raman spectra will be directed back to the spectrometer along with the sample Raman spectra, thereby interfering with the analysis.

10 The fiber optic probe for Raman analysis of United States Patent 4,573,761 issued to McLachlan, Jewett and Evans on March 4, 1986, was a substantial advance in the art of Raman spectroscopy using fiber optic probes. The probe of the '761 Patent allowed excitation light back scattered from the sample to be directed back to the detector by way of a silica based optical fiber. However, this light generated interfering silica Raman spectra 15 convolved with the sample Raman spectra. This interference is most serious when the sample is a turbid liquid, a solid, or solid particles, because such samples tend to scatter substantial amounts of light.

The fiber optic probe for Raman analysis of United States Patent 5,112,127 issued to Carrabba and Rauh on May 12, 1992, was a further advance in the art of Raman 20 spectroscopy using fiber optic probes because a filter was positioned in the path of the Raman spectra before it enters the optical fiber connected to the spectrometer. The filter was an edge filter or a notch filter which blocked the laser wavelength but passed the Raman spectra and therefore eliminated the possibility of interfering silica Raman spectra on top of the sample Raman spectra. However, the probe of the '127 Patent exposed the filter to 25 hostile sample conditions such as heat, which can deteriorate such filters.

The fiber optic probe for Raman analysis of United States Patent Application, Serial Number 08-800,366 is a further advance in the art of Raman spectroscopy using fiber optic probes because a filter is positioned after a light collecting optical fiber. This arrangement protects the filter from hostile environments and does not result in substantial interfering 30 Raman spectra from the silica in the collecting optical fiber when the Raman probe of United States Patent 4,573,761 is used. This improvement results in a fiber optic probe useful for conducting Raman spectroscopy remotely over optical fibers with minimal interference from Raman scattering within the fibers.

A semicrystalline polymer sample is illuminated with a beam of light, preferably 35 essentially monochromatic light, most preferably perfectly monochromatic light. Any source of

light suitable for Raman spectroscopy can be used, preferably a laser. However, some lasers generate enough light at other wavelength to interfere with sensitive Raman analysis. Most preferably, a laser that generates a perfectly monochromatic beam of light is used. Further, the laser light is delivered through a sending optical fiber. Sometimes additional 5 wavelengths of light are generated by Raman scatter or fluorescence within the fiber. Preferably, a bandpass optical filter is used to pass the desired wavelength through the sending fiber and filter out the other wavelengths.

Scattered light, preferably back scattered light from the semicrystalline polymer is collected into collecting optical fibers. Preferably, the light is transmitted through the 10 collecting optical fibers, focused through a rejection optical filter, further transmitted through a detector optical fiber and is focused into a light detector. The wavelength of the back scattered light is primarily the primary wavelength of the laser but also includes light at nearby wavelengths caused by the Raman effect. The rejection optical filter is selected to filter out the primary wavelength of the laser but to pass the nearby wavelengths caused by 15 the Raman effect. The rejection optical filter thus essentially eliminates interfering Raman emission from silica in the detector optical fiber.

The fiber optic probe is positioned to illuminate the semicrystalline polymer, for example, strand, pellet, film, profile, sheet, fiber, powder, or molded part online. Preferably, the probe is remotely connected to the laser and to the detector by a sending optical fiber 20 and one or more detector optical fibers. Said fibers are of appropriate length, for example ten to one hundred meters, that allow separation of the laser and the detector from the semicrystalline polymer sample. The detector is preferably a spectrometer as is well known in the art.

Although true crystalline bands are rarely available, semicrystalline polymers have a 25 number of special features which are related to morphological features in the polymer. These spectral features can be used to determine the degree of crystallinity by Raman spectroscopy. For a given semicrystalline polymer, one or more Raman vibrational bands are often observed to disappear when crystallization is inhibited, sometimes these are called 30 crystallization-sensitive vibrational bands. In other words, the crystalline-sensitive vibrational band appears for the first time when monomeric units are aggregated to form a regular conformational segment.

From a practical standpoint, the degree of crystallinity can be determined by 35 mathematically quantifying (using band areas or chemometric modeling approaches) the crystalline-sensitive band from a Raman spectrum and correlating with the degree of crystallinity determined from another method, for example, wide-angle X ray, density

measurements, DSC, etc. Another method is to determine a relative crystallinity or a crystallinity index ("CI"). Crystallinity index can be defined as the ratio of an integrated crystalline-sensitive vibrational band unique to the morphology, or polymorph, of the semicrystalline polymer (I_c) to an integrated reference vibrational band (I_r), sometimes called 5 an amorphous vibrational band. The latter is a band whose intensity is not influenced by the degree of crystallinity, tacticity, or thermal treatments, that is, it only reflects the quantity of the semicrystalline polymer:

$$CI = I_c/I_r$$

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To illustrate the practice of this invention, examples of preferred embodiments are set forth below. However, these examples do not in any manner restrict the scope of this invention.

Crystallinity of semicrystalline SPS homopolymer and SPS and para-methylstyrene 15 ("SPS/PMS") copolymer was determined by online Raman spectroscopy and DSC. The SPS homopolymer had a molecular weight ("Mw") determined by high temperature size exclusion chromatography ("HTSEC") of 250,000, a melt flow rate ("MFR" as determined by ASTM D 1238 under conditions of 300 °C and 1.2 kilograms) of 7 grams/10 minutes ("g/10 min."), a melting point ("mp") of 272 °C, and less than 5 percent by weight atactic 20 polystyrene. The PMS copolymer level was 8 percent by weight of the total weight of the SPS/PMS copolymer. The SPS/PMS copolymer had a Mw of 275,000, a MFR of 4 g/10 min., a mp of 250 °C, and less than 5 percent by weight atactic polystyrene.

SPS homo- and copolymer powder was densified in a 30 mm Werner Pfleiderer twin screw extruder at 300 °C. The extrudate exited the extruder through a 4 hole die as strands, 25 passed through the air into an ambient temperature water bath, from the water bath through the air into a Conair Model 304 pelletizer. The die holes are arranged laterally across the die resulting in a horizontal row of 4 holes. The two outside holes were slightly smaller in diameter than the two inside holes. This allowed the inside strands to be cooled more slowly than the outside strands which increased their opacity and crystallinity. The pelletizer 30 comprised a rotary knife, which transform strands into pellets. Following the pelletizer is a collecting hopper comprising a funnel shaped bottom. The pellets accumulate in the hopper before exiting the pelletizer. The hopper comprises a 6.4 millimeter ("mm") (2.5 inch) diameter quartz window towards the bottom of the funnel shaped bottom.

Off-line crystallinity measurement was determined by DSC. DSC (DuPont 2100 DSC, Model V4.0B) was performed on a sample consisting of two pellets over a temperature range from ambient temperature to 300 °C at a rate of 20 °C per minute.

Online crystallinity was determined with a 785 nanometer ("nm"), laser with 50 milliwatt output (available from SDL Laser), a fiber optic Raman probe (Kaiser Optical Systems' Mark II, operating at 785 nm), and a spectrometer to analyze the Raman scattering which consisted of a single stage spectrograph and a charge coupled device ("CCD") (Kaiser Optical Systems' HoloProbe System). The laser, Raman optic probe, and spectrograph were connected via silica optical fibers.

Online Raman measurements of SPS homo- and copolymer were taken on strands and/or on pellets. The fiber optic probe was located on a tripod. To analyze strands, the probe was aimed at strands just prior to their entry into the pelletizer. To analyze pellets, the probe was aimed pellets through the quartz window located in the bottom of the pelletizer hopper. Data was accumulated for 30 minutes on strands and two hours on pellets.

15

EXPERIMENT 1

The crystallinity of an outside strand ("SPS/PMS-o") and an inside strand ("SPS/PMS-i") of SPS/PMS was determined. Accumulation time was 60 seconds.

20

EXPERIMENT 2

The crystallinity of SPS homopolymer versus time quenched in the water bath was determined on an inside strand ("SPS-i"). The distance the SPS strands was quenched in the water bath was varied: 11.4 mm (4.5 inch), 21.6 mm (8.5 inch), 40.6 mm (16 inch), and 55.9 mm (22 inch). Accumulation time was 60 seconds. Pellet samples of the stand were collected for DSC analysis.

25

EXPERIMENT 3

The crystallinity of SPS/PMS was determined on pellets by aiming the probe through the quartz window in the pelletizer hopper. Accumulation time was 60 seconds.

30 The rate at which pellets exited the hopper was manually retarded while collecting data. Pellet samples were collected for DSC analysis.

EXPERIMENT 4

Amorphous SPS/PMS ("SPS/PMS-A") was produced by running the strands through the full length of the water bath. Increasing the time the polymer was quenched in

the water bath caused the strands to cool quickly and completely thus minimizing crystallization. SPS/PMS-A was analyzed as in Experiment 4. Pellet samples were collected for DSC analysis.

The Raman spectrum crystalline-sensitive vibrational band at 770 reciprocal centimeters ("cm⁻¹") is present with finite amounts of crystalline SPS homo- and copolymer regions. The intensity of the 770 cm⁻¹ band has been shown to be directly proportional to the degree of crystallinity. To obtain a crystallinity index, the intensity of the 770 cm⁻¹ band is integrated (using tangent baseline integration) and divided by the integrated intensity of the amorphous-sensitive vibrational band at 1000 cm⁻¹ (Table 1). For Experiments 3, 4, and 5 the Raman 770 cm⁻¹/1000 cm⁻¹ ratio (x) correlates to the percent crystallinity (y) as determined by DSC by the following equation:

$$y = 179.682x + 7.806$$

TABLE 1

Experiment	Cl, 770 cm ⁻¹ /1000 cm ⁻¹	Accumulation Time, seconds	DSC, % crystallinity
1.			
SPS/PMS-i	0.153	60	ND ¹
	0.153	60	ND
	0.155	60	ND
SPS/PMS-o	0.04	60	ND
	0.042	60	ND
	0.039	60	ND
2.			
SPS-i			
11.4 mm	0.164	60	37.75
	0.167	60	ND
	0.165	60	ND
	0.173	60	ND
21.6 mm	0.184	60	ND
	0.19	60	ND
	0.167	60	ND
	0.181	60	ND
40.6 mm	0.179	60	37.15
	0.179	60	ND
	0.172	60	ND
55.9 mm	0.103	60	31.7
	0.113	60	ND
	0.114	60	ND
3.			
SPS/PMS	0.114	60	27.37
	0.116	60	ND
	0.131	60	ND
	0.118	60	ND
	0.14	60	ND
	0.132	60	ND
4.			
SPS/PMS-A	0.01	60	7.5

¹not determined

WHAT IS CLAIMED IS:

1. A method for online measurement of crystallinity of semicrystalline polymers, the method comprising the steps of:
 - 5 (a) illuminating online a sample of the polymer with a beam of light;
 - (b) collecting scattered light;
 - (c) converting the collected scattered light to a Raman spectrum; and
 - (d) determining the degree of crystallinity using the Raman spectrum.
- 10 2. The method of Claim 1 wherein the beam of light is laser light.
3. The method of Claim 2 wherein the laser light is essentially monochromatic.
4. The method of Claim 1 wherein the scattered light is back scattered light.
- 15 5. The method of Claim 1 wherein the step of determining the degree of crystallinity comprises:
 - (i) integrating a crystalline-sensitive vibrational band of the Raman spectrum, which band is unique to a polymorph of the semicrystalline polymer, to obtain an integrated crystalline-sensitive vibrational band (I_c);
 - (ii) integrating a reference vibrational band of the Raman spectrum, whose intensity is not influenced by the degree of crystallinity of the semicrystalline polymer, to obtain an integrated reference vibrational band (I_r); and
 - (iii) ratioing I_c with I_r to determine the degree of crystallinity.
- 20 6. The method of Claim 1 wherein the steps of illuminating online and collecting scattered light are performed with a Raman fiber optic probe.
- 25 7. The method of Claim 1 wherein the beam of light illuminates a strand of the semicrystalline polymer.
- 30 8. The method of Claim 1 wherein the beam of light illuminates pellets of the semicrystalline polymer.

9. The method of Claim 1 wherein the beam of light illuminates a film of the semicrystalline polymer.

10. The method of Claim 1 wherein the beam of light illuminates a fiber of the
5 semicrystalline polymer.

11. The method of Claim 1 wherein the beam of light illuminates a powder of the semicrystalline polymer.

10 12. The method of Claim 1 wherein the beam of light illuminates a profile of the semicrystalline polymer.

15 13. The method of Claim 1 wherein the beam of light illuminates sheet of the semicrystalline polymer.

14. The method of Claim 1 wherein the beam of light illuminates a molded part of the semicrystalline polymer.

20 15. The method of Claim 1 wherein the semicrystalline polymer is syndiotactic polystyrene.

16. A method for process control of the crystallinity of a semicrystalline polymer, the method comprising the steps of:

- 25 (i) measuring online the degree of crystallinity in the semicrystalline polymer by
(a) illuminating online a sample of the polymer with a beam of light;
(b) collecting scattered light;
(c) converting the collected scattered light to a Raman spectrum;
and
(d) determining the degree of crystallinity using the Raman
30 spectrum,
and
(ii) adjusting online the crystallinity of the semicrystalline polymer according to the online measurement of crystallinity of step (i).

17. The method of Claim 16 wherein the step of adjusting online the crystallinity of the semicrystalline polymer comprises the step of controlling the temperature of the semicrystalline polymer.

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/25170

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 G01N21/65

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>KELLAR E J C ET AL: "Raman vibrational studies of syndiotactic polystyrene. 2. Use of the fundamental nul vibrational mode as a quantitative measure of crystallinity within isotropic material" MACROMOLECULES, vol. 30, no. 8, April 1997, pages 2400-2407, XP002096872 ISSN 0020-9297 see abstract</p> <p>---</p> <p>-/-</p>	1-3, 5, 9, 15

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search	Date of mailing of the international search report
17 March 1999	01/04/1999
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016	Authorized officer Johnson, K

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WESLEY IJ ET AL: "The low-temperature Fourier-transform Raman-spectrum of polystyrenes" SPECTROCHIMICA ACTA A - MOLECULAR SPECTROSCOPY, vol. 50, no. 11, October 1994, pages 1959-1966, XP002096873 ISSN 0584-8539	1-3,15
A	see abstract ---	16,17
X	CHALMERS J M ET AL: "FTIR, FT-Raman and chemometrics: applications to the analysis and characterisation of polymers" TRAC, TRENDS IN ANALYTICAL CHEMISTRY, vol. 15, no. 1, January 1996, page 18-25 XP004034796 ISSN 0165-9936	1-3,6,7, 9,10,13
A	see page 18, left-hand column - page 19, left-hand column; page 22, right-hand column, paragraph 2 - page 23, right-hand column, paragraph 2; figure 7 ---	5,8,11, 12,14,16
X	ADAR F ET AL: "Raman spectroscopy for process/quality control" APPLIED SPECTROSCOPY REVIEWS, vol. 32, no. 1-2, February 1997, pages 45-101, XP000695107 ISSN 0570-4928 see page 77, paragraph 7; page 83, paragraph 4 - page 85, paragraph 1 ---	1-3,6,7, 10,16
X	IWAMOTO R ET AL: "Determination of crystallinity of swollen poly(vinyl alcohol) by laser Raman spectroscopy" JOURNAL OF POLYMER SCIENCE, POLYMER PHYSICS EDITION, vol. 17, no. 9, September 1979, pages 1507-1515, XP002096874 ISSN 0098-1273	1-3,5,9, 13,16,17
Y	see the whole document ---	4,8,11, 12,14,15
		-/-

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	COONEY T F ET AL: "Raman spectral study of solid and dissolved poly(vinyl alcohol) and ethylene-vinyl alcohol copolymer" JOURNAL OF POLYMER SCIENCE, PART B (POLYMER PHYSICS), vol. 32, no. 7, May 1994, pages 1163-1174, XP002096875 ISSN 0887-6266	4,8
A	see page 1163, right-hand column, paragraph 2 - page 1164, left-hand column, paragraph 2; page 1168, right-hand column, paragraph 2 - page 1169, right-hand column, paragraph 2; page 1170, right-hand column, paragraph 2 - page 1171, left-hand column, paragraph 2 ---	1-3,5,9,13
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P,X	ZHANG S L ET AL: "Hyperspectral Raman line imaging of syndiotactic polystyrene crystallinity" APPLIED SPECTROSCOPY, vol. 52, no. 10, October 1998, pages 1264-1268, XP002096877 ISSN 0003-7028 see abstract -----	1